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# THE USE OF ADMIXTURES IN HIGH ALUMINA CEMENT MORTAR FOR THE MARINE ENVIRONMENT

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## SUMMARY

High Alumina Cement (HAC) mortars, made at $5^{o}$, $20^{o}$ and $40^{o}$C, were mixed using seawater, deionised water and reconstituted seawater. The admixtures used were: an accelerator, a superplasticiser, anti-washout, air-entrainment, water-proofer and an ethylene-vinyl acetate (EVA) polymer latex dispersion. Results on strength and hydrate development, permeability and chloride ion migration, and short term durability against freeze/thaw and wet/dry cycling in seawater are presented. The accelerator gave good early strengths but poor resistance to freeze/thaw. The superplasticiser gave poor resistance to freeze/thaw. Air entrainer, waterproofer, polymer latex and anti washout admixture all inhibited conversion to some extent but the latex gave poor strength and durability. Air entrainer and waterproofer gave good freeze/thaw protection even for fully converted samples. The anti-washout admixture gave poor flexural strength at one year.

## SOMMAIRE

On a fabriqué les mortiers du ciment alumineux à 5, 20 et $40^{o}$C avec l'eau de mer, l'eau pur et l'eau salée artificielle, et avec quelques adjuvants. Ici on présente des résultats du durcissement, de la conversion cristalline, du perméabilité, de la diffusion des chlorures et du durabilité contre le gélation/degélation et contre le mouillage/séchage.

## INTRODUCTION

HAC is known to have superior qualities in resisting attack by seawater and many other hostile chemical environments. HAC is widely recommended as being more durable than ordinary portland cement in seawater (1,2). Conversion does continue but is usually very slow (as little as 15% in 34 years) except in the tidal zone or in warm waters. HAC made with w/c < 0.4 has been found to be particularly resistant. Some authors have suggested that HAC mixed with seawater was more likely to lead to problems, due to formation of chloroaluminates, (3) and some that it might even be better (1). Halse and Pratt (4), for instance, found that although there was early retardation with seawater and HAC, the later microstructure was very similar to that with fresh waters.

A research programme was set up to investigate the durability of HAC mortars, mixed with sea and fresh waters and with various common types of admixtures. The aim was to provide information on the effectiveness of a range of admixtures which would be useful to those designing mixes for marine applications such as repair work. Information on the effects on fresh properties has already been reported (5); this paper reports results on hardened properties.

## EXPERIMENTAL PROGRAMME

Materials

HAC (Ciment Fondu) from a single batch supplied by Lafarge Aluminous Cement Co Ltd was used throughout with a standard graded sand. Three different mixing waters were used: de-ionised water (di), Irish Sea water, settled but not filtered (sw), and reconstituted seawater (corrosion test mixture - BDH Chemicals (rsw)), see Table 1. Each mix was made with one of the above waters alone and also containing additional sea salts in an amount intended to simulate the use of unwashed sea-won sand (di + ss, sw + ss and rsw + ss). The amount of corrosion test mixture needed to achieve this was 6.6g total solids per kg of sand in the mortar. In every case the total water/cement ratio was 0.4 and the sand/cement ratio was 1.5. The admixtures used were chosen to represent a range of types such as might be used in marine work, whether for bulk work or for repairs. The admixtures and their dosage rates were:

lithium citrate accelerator at 0.025% by weight of cement (Accel)
superplasticiser (FEB SP3) at 0.6% by weight of cement (SP)
anti-washout (Conplast UW) at 1% by weight of cement (AWO)
air-entrainer (Cormix AE1) at 45ml/50kg of cement (AEA)
water-proofer (Palace "Intrapruf") at 1:30 in the mixing water (WP)
EVA dispersion polymer (Vinamul 3281) at 5% solids by weight of cement (EVA).

In each case the proportions used were the maximum recommended by the manufacturer. Including the nil admixture this programme resulted in a factorial design of 126 mixes (7 admixtures x 3 waters x 3 temperatures x 2 aggregate salts content).

Table 1. Composition of sea waters (ppm by weight of each species)

| Species | $Cl^-$ | $Na^+$ | $SO_4^=$ | $Mg^{2+}$ | $Ca^{2+}$ | $K^+$ | $CO_3^=$ | $Br^-$ |
|---|---|---|---|---|---|---|---|---|
| Sea Water (sw, Irish Sea) | 19000 | 10500 | 2650 | 1350 | 400 | 380 | 160 | 65 |
| Reconstituted (rsw) | 16200 | 9960 | 1830 | 570 | 440 | - | - | - |

Mixing and test methods

The materials, except for admixtures, for each mix were brought to the temperature (5, 20, 40°C) at which they would eventually be cured. Each batch of about 5kg was dry mixed, in a Kenwood Chef domestic mixer, at 120 rev/min for 1 minute, then 1 minute of hand mixing with the mixing water plus admixture, followed by 1 minute at 250 rev/min.

The following test methods were used:
Early strength - The ultrasonic pulse velocity (UPV) by the PUNDIT instrument, hardness by Schmidt

rebound hammer and crushing strength of 75mm cubes were measured at 7 and 28 days.
Hydrate composition and conversion - Finely ground samples from crushed cubes were tested by Derivative Thermogravimetry using a Stanton Redcroft TG750 instrument.
Water permeability - The Figg procedure (6) was carried out on a cylindrical specimen 40mm diameter by 120mm long using a 10 mm hole drilled in one end.
Chloride ion migration - This was observed in a multi-sample system set up to allow chloride ions to migrate from a reservoir containing rsw through 3mm thick discs cut from 40mm diameter specimens into a chamber containing di water. The changing chloride ion concentration in the latter was monitored by repeated tests with an ion selective electrode and the diffusion coefficient calculated from the slope of the line of concentration against time.
Durability - A laboratory programme of wet/dry and freeze/thaw cycling was carried out in di water, sw and rsw. After 7 days curing in the temperature controlled tanks, each specimen (prisms 160 x 40 x 40mm) received 120 cycles spread over a 12 month period during which it stood in water to depths of alternately 25 or 100 mm (wet/dry) or in water to a constant 100mm depth but alternately frozen at -5°C and thawed at +20°C. UPV, Schmidt hardness, weight loss and length change were recorded at intervals over the year's exposure, together with visual assessment. At the end of the year each specimen was tested for flexural strength. In addition a long term exposure trial has been established in a west coast marine site, but this will form the subject of a future paper.

## RESULTS

A large amount of data has been accumulated and space permits only selected significant features to be presented here. Analysis of Variance was carried out to assess the significance of the factors in the factorial design and only those factors found to be significant are described. In this context significant means that there is a less than 1% probability that the effect mentioned is due to chance.

### Early strength

Admixture, temperature and the interactions between them had a statistically significant effect on compressive strength, UPV and Schmidt hardness at 7 and 28 days. Additionally water had a significant effect on compressive strength only. Fig. 1 shows the pattern of 28 day cube strengths. Strengths at 20°C were nearly always higher than those at 5°C with 40°C being lowest of all. The same pattern was seen for the UPV and Schmidt hardness.

### Hydrate composition

Admixture, temperature and the interaction between them were the only significant effects on the degree of conversion. There was no difference between the results after 7 and 28 days curing. Fig. 2 shows the results averaged over all six mixing waters.

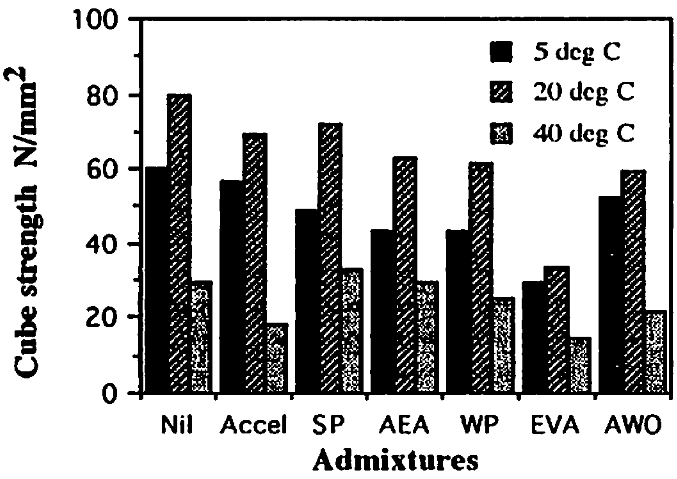



Fig. 1. Effect of admixtures on 28 day cube strength (averages over all waters).

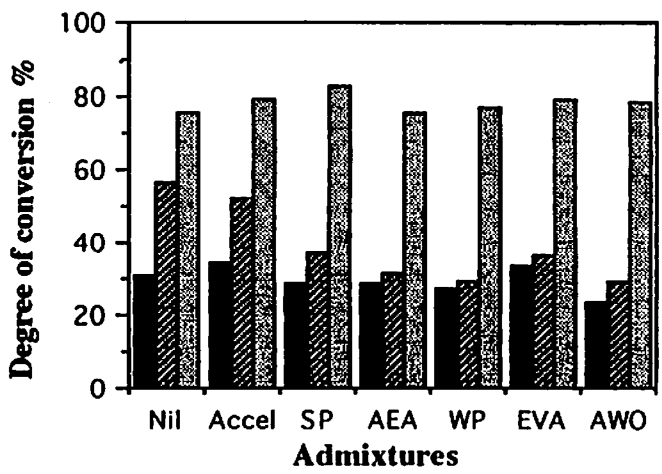
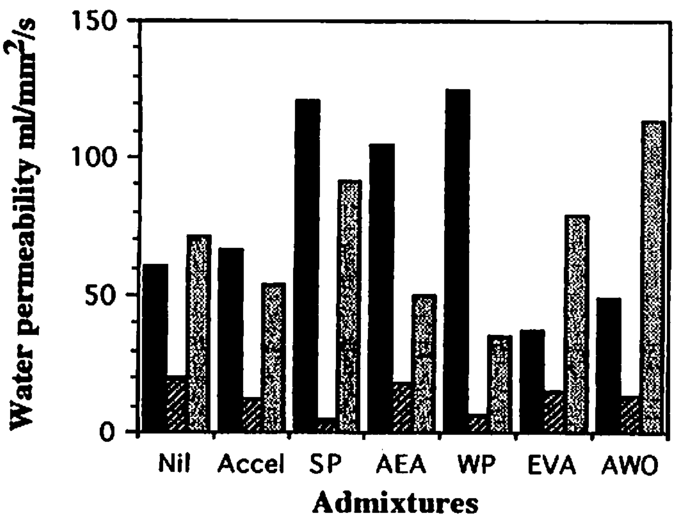



Fig. 2. Effect of admixtures on the degree of conversion at 28 days (averages over all waters)



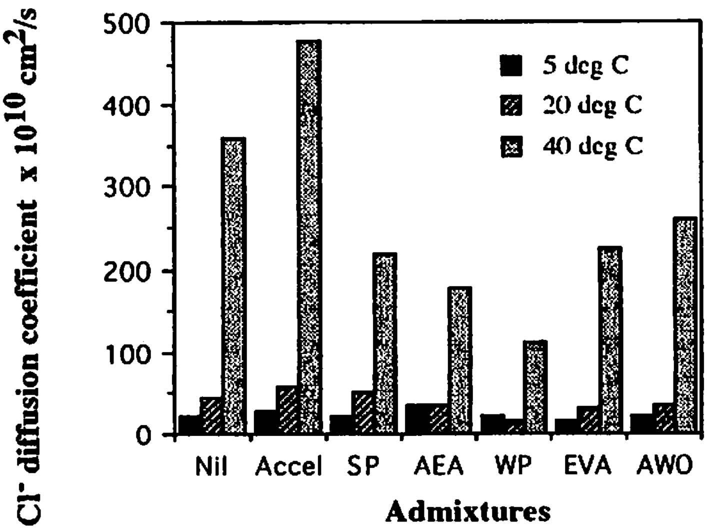




Fig. 3 Effect of admixtures on water permeability (averages over all waters).

Fig. 4 Effect of admixtures on chloride diffusion (averages over all waters).

Water permeability

Temperature was the only significant effect on water permeability. Fig. 3 shows the results averaged over all six mixing waters.

Chloride migration

Admixture, temperature and the interaction between them were the only significant effects on chloride ion migration. Fig. 4 shows the chloride diffusion coefficient averaged over all six mixing waters.

Short term durability testing

Flexural strength after one year - Four way Analysis of Variance shows that the effects of the various factors on flexural strength are complex. Temperature, admixture, water and exposure regime were significant at the 1% level, as were every two- and three- factor interaction except mixing water/ exposure regime and admixture/ mixing water/ exposure regime. Table 2 shows the effect of freeze/thaw and wet/dry cycling on the flexural strength after one year.

Weight and length changes - All specimens gained in weight during the wet/dry cycling and only those containing accelerator lost weight through spalling under freeze/thaw cycling in sw and rsw. Experimental difficulties resulted in too much missing data to allow Analysis of Variance to be done on length change.

Mortars containing superplasticiser, waterproofer, EVA and anti washout admixture made at 5°C tended to contract, while the remainder expanded.

## DISCUSSION

Table 3 summarises the findings relating to the effects of admixtures, mixing temperatures and environment. The effects of the admixture types varied according to the test under consideration, but generally the EVA polymer dispersion performed poorly across a wide range of parameters. Air entraining agent, waterproofer, EVA and anti washout all offered some protection against conversion and also against spalling in freeze/thaw, but this is not reflected in an improved strength at a later age when compared with the

Table 2 Flexural strength ($N/mm^2$) of prisms after 1 year of freeze/thaw exposure.

| Mix water | Temp °C | Nil | Accel | SP | AEA | WP | EVA | AWO |
|---|---|---|---|---|---|---|---|---|
| | | **Exposed to DI water** | | | | | | |
| DI | 5 | 5.7 | 4.2 | 5.5 | 4.4 | 4.2 | 6.1 | 6.1 |
| | 20 | 7.9 | 9.8 | 7.7 | 7.9 | 8.1 | 7.8 | 8.2 |
| | 40 | 7.8 | 5.7 | 5.7 | 7.6 | 5.0 | 4.3 | 5.0 |
| SW+SS | 5 | 4.1 | 4.8 | 3.9 | 4.1 | 4.2 | 6.2 | 7.0 |
| | 20 | 6.1 | 7.7 | 6.2 | 5.5 | 7.5 | 8.7 | 6.0 |
| | 40 | 6.4 | 5.3 | 8.7 | 8.2 | 6.4 | 6.5 | 4.3 |
| | | **Exposed to seawater (SW)** | | | | | | |
| DI | 5 | 7.0 | 8.7 | 7.5 | 4.9 | 4.2 | 7.2 | 8.0 |
| | 20 | 7.5 | 10.5 | 6.7 | 6.2 | 6.4 | 7.3 | 8.0 |
| | 40 | 6.9 | 6.4 | 5.5 | 7.5 | 7.3 | 4.3 | 5.5 |
| SW+SS | 5 | 7.6 | 7.2 | 4.3 | 4.8 | 5.3 | 4.6 | 7.7 |
| | 20 | 5.7 | 4.2 | 6.0 | 5.3 | 5.7 | 5.9 | 4.8 |
| | 40 | 8.1 | 5.8 | 8.5 | 8.6 | 8.7 | 6.0 | 5.5 |
| | | **Exposed to reconstituted seawater (RSW)** | | | | | | |
| DI | 5 | 6.1 | 6.9 | 5.9 | 4.8 | 4.4 | 6.8 | 7.3 |
| | 20 | 7.8 | 9.5 | 6.4 | 6.3 | 7.1 | 7.5 | 8.6 |
| | 40 | 7.3 | 7.2 | 6.2 | 7.3 | 7.0 | 4.4 | 4.3 |
| SW+SS | 5 | 4.1 | 4.3 | 4.8 | 4.0 | 4.8 | 5.3 | 5.1 |
| | 20 | 5.6 | 7.6 | 6.3 | 5.4 | 5.5 | 7.0 | 6.1 |
| | 40 | 8.2 | 4.3 | 8.4 | 7.8 | 8.3 | 6.9 | 5.1 |

nil, accelerator and superplasticiser. Although the strength of the mixes was not as good as for the nil admixture, anti washout admixture gave very good protection against spalling in freeze/thaw and was some use in preventing washout. The superplasticiser did not give the dramatic increase in workability that would be expected in portland cement mixes, but seemed to offer other benefits: good cube and flexural strengths with some increase in flow but a similar setting time to the control. The accelerator also gave good results despite high conversion levels. It should be noted that only in the cases of the accelerator and superplasticiser had previous research considered the suitability or otherwise of the admixture for use with HAC and in most cases only anecdotal evidence was available.

As expected, temperature of mixing and curing is very important in both the early and long term performance of HAC. HAC exposed to 40°C is highly converted and other results such as strength are highly dependent on the level of conversion and the effects of other variables are largely swamped by the effect of conversion. Somewhat more surprisingly the 5°C samples, with their very low early conversion levels, did not perform correspondingly well in all tests. They performed badly in the laboratory durability trials, with spalling, poor flexural strength and high water permeability. Further work will be needed to investigate this unexpected behaviour, but later, unexplained, conversion may have played a part.

Mixing water type rarely produced significant effects but there is some evidence that a slight reduction in strength occurs with salt waters. It was slight and might not be a problem if fresh water was not readily obtainable, providing the potential problem of reinforcement corrosion is addressed.

The freeze/thaw cycling clearly had a more deleterious effect on the samples than the wet/dry cycling, but there seemed to be less of an effect due to the type of water in which the samples were stood. Salt waters appeared to lead to more spalling within the freeze/thaw groups but not in the wet/dry tests.

## CONCLUSIONS

This comprehensive study has shown that the effects of admixtures are so complex that potential users of high alumina cement in the marine environment must carry out trials on any admixture which is being considered for use. Such trials must take place in the actual conditions which the material will face in practice.

Table 3 Summary of influences on test results

| Test parameter | Nil | Accelerator | SP | Admixture types AEA | WP | EVA | AWO |
|---|---|---|---|---|---|---|---|
| Chloride diffusion | - | v.high at 20°C | - | low at 5 and 40°C | low at 40°C | - | - |
| Conversion | high at 20°C | high at 20°C | - | inhibited | inhibited | inhibited | inhibited |
| Cube strength | high | high | high | medium | medium | low | medium |
| UPV 28days | high | high | medium | medium | medium | low | medium |
| Hardness | hard | hard | hard | medium | medium | soft | medium |
| Flexural strength 1 year | - | good | good | - | - | - | poor |
| Weight change | loss in freeze/ thaw in SW and RSW | loss in freeze/ thaw in SW and RSW | loss in freeze/ thaw in RSW | - | - | - | - |
| Visual | - | 20°C mixes spalled in freeze/thaw | 20°C mixes spalled in freeze/thaw | 40°C mixes v.good in freeze/thaw | 40°C mixes v.good in freeze/thaw | - | 5°C mixes v.good in freeze/thaw |

| Test parameter | Mixing temperature 5°C | 20°C | 40°C |
|---|---|---|---|
| Chloride diffusion | low | medium | high |
| Water permeability | high | medium/low | high |
| Conversion | low | medium | high: dominates all effects |
| Cube strength | medium | usually highest | lowest |
| UPV | medium | high | low |
| Hardness | medium | hardest | softest |
| Flexural strength after 1 year | generally low in freeze/thaw but often high in wet/dry | usually best in freeze/thaw but poor with added salt | usually poor when DI used but good with added salt |
| UPV over 1 year | usually highest and still rising, especially for nil and accelerator | slightly rising trend | started lowest but rose steeply apart from nil which was falling at 1 year |
| Length change | contracted | expanded by variable amounts | expanded by variable amounts |
| Visual | most except AWO were etched in freeze/thaw | some early spalling in freeze/ thaw with accel and SP | some spalling in both freeze/ thaw and wet/dry |

| Test parameter | Environment Freeze/thaw in: DI | SW | RSW | Wet/dry in: DI | SW | RSW |
|---|---|---|---|---|---|---|
| Flexural strength | rarely exceeded 8 N/mm$^2$ | | | good results for 20°C mixes: many >8N/mm$^2$ | | |
| Weight change | - | loss | loss | gain | - | most gain |
| Visual | beige/brown below water line | grey, spalling | grey, spalling below water line | beige/brown | grey | grey |

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